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(56) Documents cited

**GB A 2134930 GB A 2110246 GB 1342072  
GB A 2130795 GB 1352241**

(58) Field of search

**C7F  
Selected US specifications from IPC sub-class C23C**

(54) **Coating machine parts and tools with high hardness material**

(57) Machine parts and tools, preferably of temperature sensitive steels, are coated with high hardness material of nitrogen and carbon compounds of metals of the group Ti, Zr, Hf, Cr, Ta, W and Nb by reactive cathodic atomisation of at least one of the said metals in a nitrogen or carbon-containing atmosphere under atomisation conditions. To solve the problem of applying thick, fault-free coatings to temperature sensitive substrates, intermediate metallic layers of at least one of the metals from the group Ti, Zr, Hf, Cr, Ta, W, Nb; Al, Ni, Fe are applied under non-reactive conditions by cathodic atomisation between the individual layers of high hardness material from the group TiN, TiC, TiCN; ZrN; HfN; CrN; Cr<sub>2</sub>C<sub>3</sub>; TaC, TaN; WN, WC; NbN constituting only a fraction of the total coating thickness.

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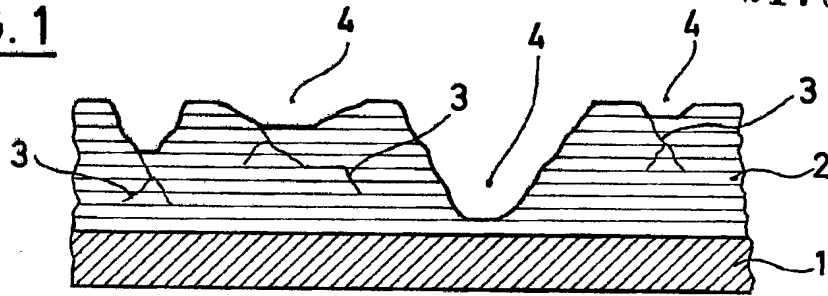
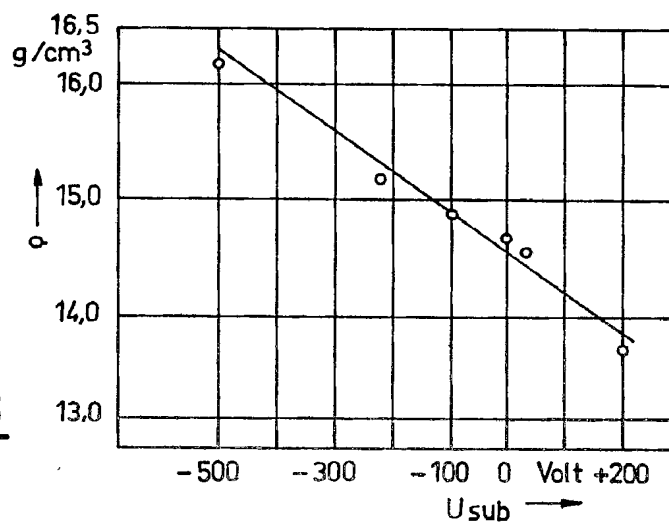
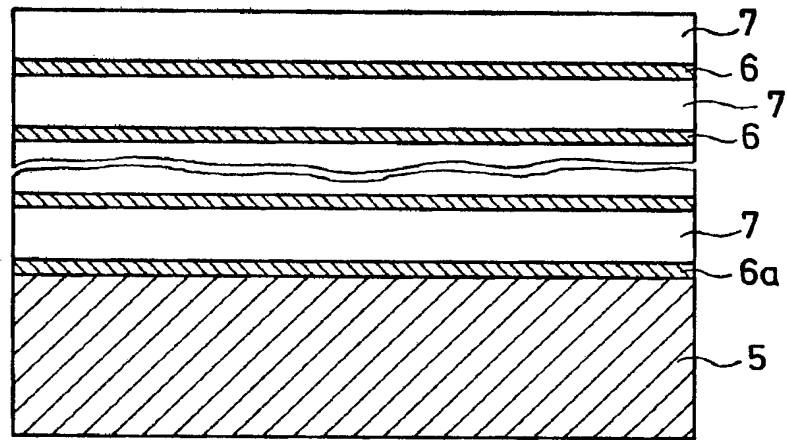
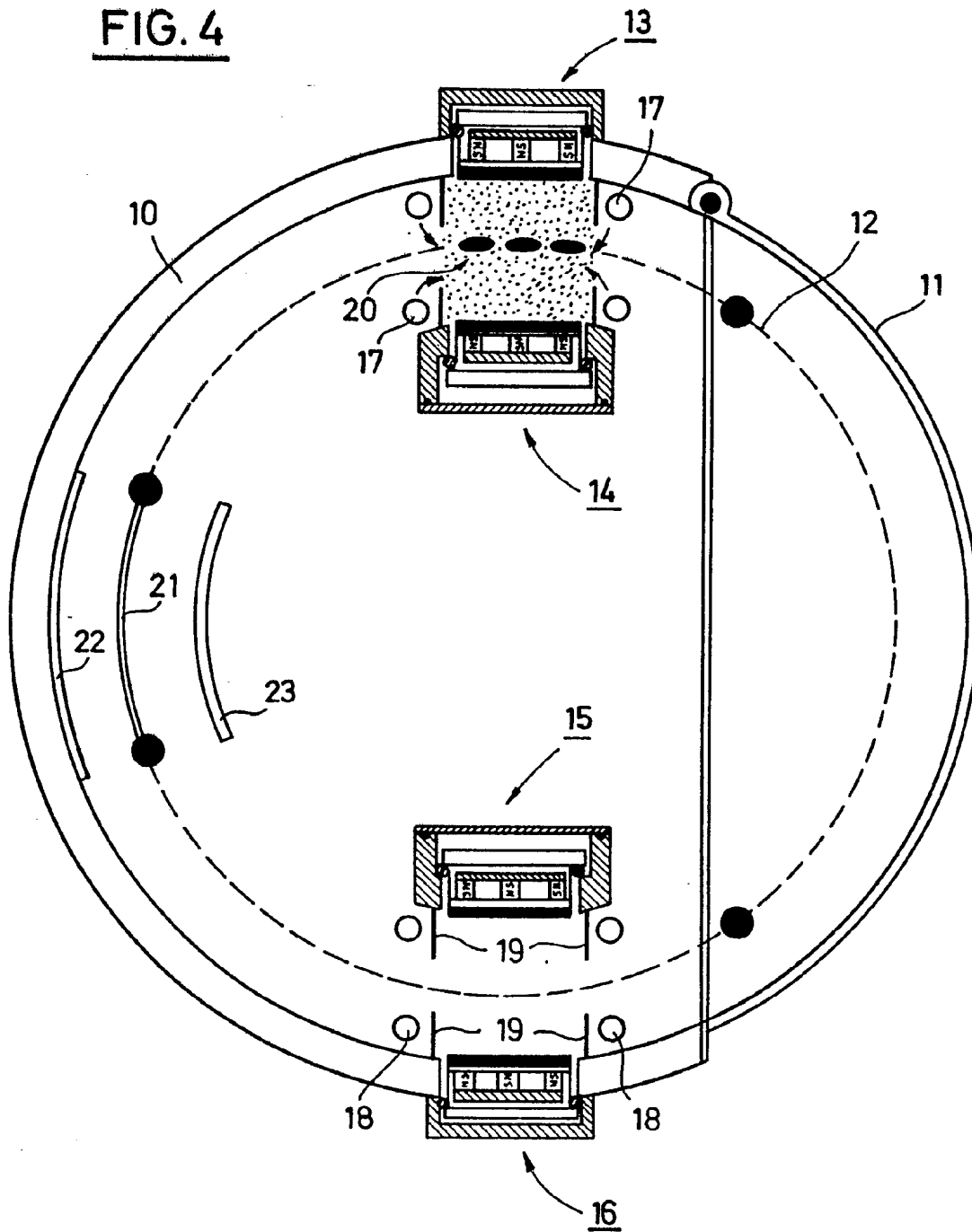
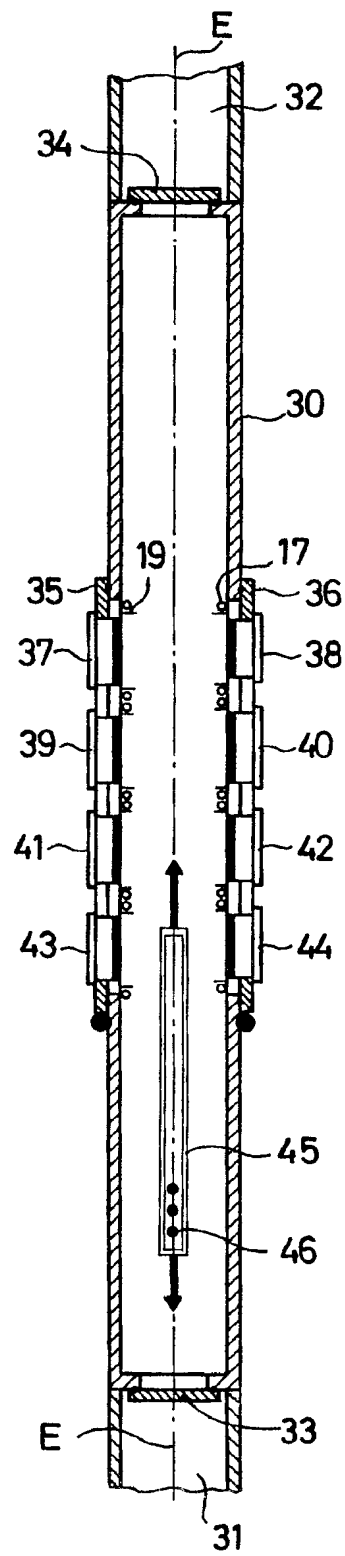
FIG. 1FIG. 2FIG. 3

FIG. 4

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FIG. 5

## SPECIFICATION

**Process for coating machine parts and tools with high hardness material and machine parts and tools produced by the process**

- 5 The invention relates to a process for coating machine parts and tools and the like with high hardness compounds. 5
- Such a process and also an apparatus suitable therefor are described in DE-OS3107914 and corresponding US-PS4426267 which describe passing the base bodies of tools and workpieces 10 through an arrangement of atomising cathodes. Even if one passes the base bodies of machine parts and tools, that is to say the substrates to be coated, several times through the known arrangement of atomising cathodes, there results a plurality of directly adjacent layers of like composition of which the interfaces can just be seen under the electron microscope, but which as a whole can be regarded as a monolithic coating system, even though it is built up from 15 individual layers. 15
- Hard, wear-resistant coatings for the surfaces of cutting tools, shaping tools or machine parts subject to wear are at present produced inter alia by ion-plating. The best-known coatings comprise TiN, TiC, TiCN, HfN, CrN, TaC, TaN, WC, W<sub>2</sub>N and NbN. In ion-plating various processes are used which differ principally in respect of the source of coating material used. 20 Technical solutions are known with thermal vapourisers in the form of vapourising vessels, electron beam vapourisers, hollow cathode systems, arc vapourisers and cathode atomising systems. The present invention is concerned with the process of ion-plating by cathode atomisation. 20
- Wear resistant, life-increasing coatings, for example on twist drills, are at present between 2 25 and 5  $\mu$ m or 2000 to 5000nm thick. To achieve a satisfactory bonding and density of the coating structure, such coatings are applied to substrates which are heated to temperatures between 300 and 500°C. It is important that these parts are maintained throughout the whole coating process at the most constant temperature level possible of for example 450°C. This can be done for example by letting the substrate remain continuously in the plasma in the coating zone, 30 by which the ion bombardment important for the ion-plating can be maintained uniform. These requirements are also to be taken into consideration in presently used coating processes. 30
- If one accepts large temperature differences during coating, which can happen if the substrate is taken out of the region of ion bombardment during the coating process, an inhomogeneous layer build up occurs in respect of the brittleness of the high hardness material concerned, its 35 hardness and its internal stresses, which chiefly leads to micro-fissuring and to laminar separation of the coating. If a tool so coated is used to work a workpiece, the strains imposed by temperature variations lead to destruction of the coating if it is not sufficiently homogeneous. 35
- The disadvantageous effects described occur above all if the coating is carried out at a temperature lower than the temperature range mentioned. As has been shown in the application 40 of decorative coatings to temperature sensitive components such for example as watch cases of brass, a reasonable coating is possible at lower temperatures if the coating is carried out stepwise or the coating is built up from individual layers. Such a process is also described in DE-OS3107914 already mentioned. By multiple passes of a substrate secured to a rotary substrate holder, it can be further cooled down after emerging from the coating zone so that a 45 maximum temperature of some 200 to 250°C will not be exceeded. The known process has been proved in the production of gold coloured coatings of TiN, as those coatings have a maximum thickness of some 1  $\mu$ m or 1000nm. Experiments have shown however that the increase in coating thickness to values of 2000nm to 5000nm, as is required for technical applications, leads to the problems described above, namely that the coating has micro-fissuring 50 so that it suffers the flaking-off of surface layers described. This cannot be tolerated in machine components subject to heavy mechanical loading or tools, as the mechanical forces will lead very quickly to widespread flaking-off of the coating structure which anyway has micro-fissure damage. 50
- The possibility of using functional, i.e. technically useful high hardness material layers is 55 substantially improved if it can be achieved that the substrate temperatures in the coating process are limited to values between 150 and 200°C and then coating thicknesses of 2000nm and above are produced. In such a case tool steel, as is required for cutting and shaping tools, machine parts subject to friction such for example as thread guides in textile machines and even plastic parts can be coated with high hardness material. 55
- 60 The invention is based on the problem of specifying a process of the kind described in which temperature sensitive substrates can be used and which is suitable also for the production of relatively greater coating structure being at risk of micro-fissuring and/or high internal strains. 60
- The invention comprises a process for coating machine parts and tools, preferably of temperature sensitive steels, with high hardness materials of nitrogen and carbon compounds of metals 65 from the group Ti, Zr, Hf, Cr, Ta, W and Nb by reactive cathodic vapourisation of at least one 65

of the said metals in a nitrogen or carbon containing atmosphere under atomisation conditions, wherein metallic intermediate layers of at least one metal from the group Ti, Zr, Hf, Cr, Ta, W, Nb; Al, Ni and Fe are applied by cathodic atomisation under substantially non-reactive conditions between individual layers, comprising each only a fraction of the total coating thickness, of high hardness material from the group TiN, TiC, TiCN; ZrN; HfN; CrN, Cr<sub>2</sub>C<sub>3</sub>; TaC, TaN, WN, WC and NbN.

By the separation according to the invention of the individual layers of high hardness material by the said metallic intermediate layers, hard coatings can be produced at relatively low substrate temperatures, for example below 200°C, which are not liable to flaking even with greater coating thicknesses over some 2000nm. As examination under the electron microscope has shown, micro-fissuring is avoided, and it can be taken that internal stresses, which otherwise increase with increasing thickness are precluded by the higher ductility of the metallic intermediate layers.

The term "metallic intermediate layer" does not exclude a slight proportion of reaction products of the relevant metal with the atmosphere inside the coating apparatus. It is sufficient that the metallic intermediate layer has a substantially metallic, thus a ductile character and a reducing effect on the adjacent high hardness material. Ideally, naturally, a pure metal intermediate layer should be sought for.

In the choice of metal for the intermediate layers, what matters is to get sufficient bonding with respect to the adjacent material (interface). It is in addition desirable that the material of the intermediate layer has in respect of the adjacent material, as already noted, a reducing effect. To explain this effect it is noted that the substrates in the production of the individual layers are necessarily taken at a relatively high temperature out of the coating zone and thus find themselves in an atmosphere which comprises, at least partially, activated gas molecules. As the so called residual gas atmosphere in coating apparatus contains as a rule traces of very reactive acids, this leads to the formation of thin oxide films on the individual layers by which not only the coating homogeneity of the coating packet but also the internal content of the coating packet is disturbed. This effect can in any event be substantially compensated for by a reducing effect of the metal of the intermediate layer, if not completely eliminated.

It is finally desirable for the metallic intermediate layer to have a high thermal conductivity. In a high, especially a local temperature variation loading, as happens principally to cutting tools, there arises in the high hardness material layer itself a heat concentration which naturally also leads to corresponding thermal stresses. By a corresponding thermal conductivity of the metallic intermediate layers can be effected very substantially the reduction of the temperature differences and thus thermal stresses.

It has been shown that the metals suggested for the intermediate layers completely solve the problem as stated. Thus layers of these metals can be alternated with the reaction product of the same metal forming the high hardness material. It is here possible to atomise the same metal, which for atomisation purposes is provided in the form of a target plate for fixing on an atomising cathode, alternately in reactive and non-reactive atmospheres. The carrying out of the process is in this way substantially simplified. It is however possible also to use aluminium, nickel and iron for the intermediate layers, thus metals which are not used for the formation of high hardness material layers.

Of especial importance is the deposition of metallic intermediate layers by cathode atomisation with the application of a correspondingly high negative potential to the substrate, that is to say, ion-plating. It will be shown with reference to a diagram that with increasing negative potential the density of the deposited coating material increases and indeed up to practically the theoretical maximum possible density. By such a measure the strength of the metallic intermediate layers is at the same time substantially increased so that the strength of the whole coating packet is likewise increased.

Of special importance is furthermore if the metal of the intermediate layers has a particularly low melting point, in any event in relation to the melting point of the high hardness material. It has in fact been shown that dense coatings of metals with relatively high melting points, similar to those of the high hardness materials themselves, are only produced if there is an ion bombardment during the cathode atomisation process. With intermediate layers with relatively low melting points the atomisation process can be carried on with a substantially lesser proportion of ion bombardment, i.e. with a lower negative substrate potential. This also has the advantage that in addition the resultant substrate temperature can be lowered, because the substrate heating is in general proportional to the size of the (negative) potential and thus to the ion bombardment.

It is self-evidently necessary that the coating packet according to the invention also has an extraordinarily adhesive connection with the base material or substrate. As the metallic components of the high hardness material layers are by their nature good bonding agents in relation to most substrate materials, in particularly in relation to metals, it is, in building up the coating according to the invention, especially advantageous so to proceed that a pure metallic layer is

first deposited on the substrate surface from the metallic component of the high hardness material in a non-reactive atmosphere and this layer then carries over in a continuous transition into the actual high hardness material layer by gradually admitting the appropriate reaction gas.

As reaction gases, nitrogen itself is considered for forming the nitride, and for forming the carbide, a light, volatile saturated or unsaturated hydrocarbon such as acetylene. For the production of so-called carbo-nitrides are considered also mixtures of nitrogen and hydrocarbon compounds. The principal component of the atomisation atmosphere is comprised of an inert gas, preferably argon. The composition of such atomisation atmospheres is however part of the state of the art, and it will not be gone into further here.

In the production of coating packets according to the invention there are basically three possible process types. In this it is already presupposed that the coating process is carried on simultaneously on opposite sides of the substrate, and that therefore the atomising cathodes are used arranged in pairs, as described in DE-OS3107914:

1. By using only one cathode pair the metallic layers and the high hardness material are produced by cyclically interrupting the gas supply. The suction of the vacuum pumps necessary in any event for the coating apparatus will be in general adequate to rid the atomisation atmosphere quickly enough of reactive gas components.
2. When using two cathode pairs, these can have attached the same target material, and one cathode pair can be used in one atmosphere of reaction gas, while the other cathode pair are used in a non-reactive atomisation atmosphere.
3. When using two cathode pairs it is possible to mount different materials on them and use on the other hand one cathode pair in reactive atmosphere and the other in non-reactive atmosphere.

If two cathode pairs are series connected there are again two basic possibilities for substrate motion. It is possible to move the substrates to and fro between the cathode pairs. It is furthermore possible, with the two cathode pairs. It is furthermore possible, with the two cathode pairs arranged in the path of a circular track of a substrate holder to cause the substrates to move one after the other with the same sense of rotation and as many times as desired through the two cathode pairs. The last described manner of operation will be explained in more detail with regard to an exemplary embodiment.

For the metallic intermediate layers can for example also be used layers of metal alloys such for example as:

Ti/Al; Ni/cr/Fe; Cr/Al; Ta/Al

Preferred layers sequences are as follows:

TiN-Al-TiN-Al-...

CrN-Cr-CrN-Cr-...

TaN-Ti/Al-TaN-Ti/Al-...

The number of regularly alternating layers is not limited upwardly. In practice, 2 to 100 high hardness material layers can be considered for the given combinations, which can be separated by 1 to 99 metal layers of the quoted metals and/or alloys. It has appeared to be particularly advantageous however for each coating packet to comprise 15 to 40 layers of high hardness material and 14 to 39 metallic layers.

The thickness of the individual layers of high hardness material can be chosen to be between 50 and 1000nm, the thickness of the individual metal layers between 5 and 100nm.

It is particularly advantageous to give the metal layers a lesser thickness than the layers of high hardness material. Thus the ratio of the layer thicknesses of the individual layers of high hardness material to those of the individual metal layers lie particularly advantageously between 10:1 and 10:5. Very well reproducible ratios have been achieved with layer thickness ratios about 10:2.

The invention also relates to tools or machine parts coated by the processes described. The invention will be further explained below with reference to Figs. 1 to 5.

These show:

Figure 1 a section through a prior art coating packet perpendicular to the substrate surface,

Figure 2 a section like Fig. 1, but to a larger scale, through a coating system according to the invention,

Figure 3 a diagram showing the dependence of the density of a metallic layer on the level of negative substrate potential  $U_{sub}$  in cathode atomisation (ion plating),

Figure 4 a horizontal section through a coating apparatus with a rotary substrate holder, and

Figure 5 a horizontal section through a coating apparatus with an oscillating substrate holder.

Fig. 1 shows a substrate 1 of a tool steel, for example of HSS quality. On this substrate, individual layers of high hardness material 2 have been deposited directly on top of one another

according to a process described in DE-OS3107914. Through a sufficiently large coating thickness, as is needed for tools (drills) (2000 to 5000nm) are seen within the coating packet not only micro-fissures 3 but also local flaking 4, the occurrence of which is substantially encouraged by the micro-fissures 3.

5 Fig. 5 shows a substrate 5 of the same tool steel on which in alternating sequence metallic intermediate layers 6 (of aluminium) and high hardness material layers 7 (of CrN or TiN) are arranged. The lowermost metallic intermediate layer 6a serves at the same time as a bonding agent. A coating produced according to Fig. 2 has for example in total 60 individual layers, namely 30 high hardness material layers 7, 29 metallic intermediate layers 6 and a bonding layer 6a.

10 In Fig. 3 the substrate potential  $U_{\text{sub}}$  in volts is on the abscissa and the density in  $\text{g/cm}^3$  on the ordinate, this for the metal tantalum and a coating thickness of 6  $\mu\text{m}$  or 6000nm. The substrate temperature was held constant for all measurements. It is seen that the density of the deposited material, starting from a positive substrate potential of 200V up to a negative substrate potential of -500V increases by almost 20%, which is of quite decisive significance for the tensile and shear strength of the material. (Ref: Mattox, D.M.; Kominiak D.V. "Structure Modification by Ion Bombardment during Deposition", J.Vac. Sci.+Techn., Vol. 9, Nr. 1, 1972, page 528).

15 In Fig. 4 is shown a horizontal section through a substantially rotationally symmetrical reaction chamber 10, which in its front part has a door 11. In the reaction chamber, a substrate holder 12 is supported for rotation about its vertical axis, which in the present case is formed as a hollow cylindrical rotary cage. The substrate holder 12 is connected through a capacitor, not shown here, to a source of potential, also not shown. On each side of the path in which the substrate holder 12 rotates is arranged in practically mirror symmetrical arrangement a pair of double cathodes 13/14 or 15/16. Each one of these magnetron cathodes is realised in the usual way; a concentric arrangement of permanent magnets SN/NS is contained in a water-cooled hollow body of non-magnetic material, of which the permanent magnets have their poles oppositely arranged as shown in the drawing. The rearward ends of this permanent magnets are connected together by a yoke plate. On the end wall of the hollow body is secured a plate-like target which consists of a metal which forms either the component of the high hardness material layer or metallic layer. The front face of this target and the substrate holder 12 are directed substantially parallel to one another. In the illustrated magnetron cathodes are elongate cathodes whose lengthwise axis runs normal to the plane of the drawing.

20 In the neighbourhood of the magnetron cathodes 13 to 16, gas inlets 17 or 18 are provided through which the noble and/or reaction gas is introduced into the reaction zone concerned. The extent of the plasma (shown by dots in the upper part of Fig. 4) is in addition limited by blinds 19 which however leave a sufficient space free for the passage of the substrates 20, of which only three are shown here schematically.

25 A blind 21 is also fixed on part of the periphery of the substrate holder 12, serving for pre-atomisation, which can be swung in between two etching blinds 22, 23. Further features of a rotary substrate holder in combination with a double cathode arrangement are described in DE-OS3107914. The apparatus there illustrated is provided however exclusively for the process of cathode atomisation.

30 The apparatus according to Fig. 4 can also be modified thereover in that the inner magnetron cathodes 14 and 15 can be removed and the substrate holder replaced by a drum-like substrate to be coated (rollers for copying machines and matrices), which rotate during the coating.

35 While Fig. 4 shows a cathode atomisation device for batch operation (the reaction chamber must be opened to atmosphere for loading), Fig. 5 shows an elongate reaction chamber 30 which can be used in quasi-continuously running process. This reaction chamber has vacuum connections 31 and 32 which are separated or separatable from the reaction chamber by valves 31 and 32. The reaction chamber 30 has doors 35 and 36 on opposite sides, in which superimposed cathode pairs 37/38, 39/40, 41/42 and 43/44 are installed. To each of these cathode pairs is arranged in addition a gas inlet 17 and blinds 19 as in Fig. 4. In the plane of symmetry E-E of all the cathode pairs a substrate holder 45 is movable, which is constructed of a framework. The principal plane of this frame runs perpendicular to the plane of the drawing. In the individual stages of this frame are inserted a plurality of substrates 46 of which only three are shown by way of example.

40 By attaching different targets (shown by thick black lines) to the cathode pairs and/or differently supplying the individual cathode pairs with inert gas (argon) and reaction gas as well as shutting off the individual reaction zones between the cathode pairs by the blinds 19 in conjunction with an oscillating motion of the substrate holder in the direction of the two arrows, the above described coating packet can be built up alternately.

45 The operating parameters for the apparatus of Figs. 4 and 5 are, including the current supply system for the magnetron cathodes or cathode pairs, prior art so that further discussion here is not required.



*Example 1:*

In an apparatus according to Fig. 4, the cathode pair 13/14 had targets (thick black lines) of titanium affixed, while the diametrically opposite cathode pair 15/16 had aluminium targets. As substrates were used threadguides of CK 15 steel with an initial temperature below 200°C, which were inserted into the substrate holder 12.

According to the known initial cleaning procedure, the coating region between the magnetron cathodes 13 and 14 was supplied via the gas inlet 17 with a mixture of argon and nitrogen, while the coating region between the magnetron cathodes 15 and 16 is supplied with pure argon via the gas inlet 18. After striking the glow discharge between the individual cathode pairs the substrate holder 12 undergoes in total some 30 rotations. By corresponding adjustment of the specific atomisation rates at the target faces in conjunction with a corresponding rotation of the substrate holder 12, such a dwell time of the substrates within the cathode pairs is attained that the coating thickness of the thus formed TiN-layers reached 50nm and the coating thickness of the thus formed Al-layers reached 10nm. There were formed altogether 30 layers of TiN and 30 layers of Al, of which 29 functioned as intermediate layers, while the lowermost formed a bonding agent to the substrate. Despite a total coating thickness of 3600nm the thread guides had extraordinary durability under normal usage conditions without any flaking being observed at the places subject to high wear.

*Example 2:*

In an apparatus according to Fig. 5, the cathode pair 37/38 had targets affixed of a TiAl alloy, while the remaining cathode pairs 39/40, 41/42 and 43/44 had titanium targets affixed. The cathode pair with the TiAl targets were supplied with inert atomising gas (argon) in the manner already described, while the tantalum targets were supplied with a reactive mixture of nitrogen and argon. With roughly equal atomising current at all cathode pairs there is produced on the basis of the surface proportions in the ratio 3:1 a corresponding layer thickness distribution between the TaN-layers and the Ti/Al-layers. The alternating layer sequence is here achieved by the oscillating motion of the substrate holder 45. Here too is produced a satisfactory durability of the stampings used as substrates without flaking being observed in the regions of edges subject to heavy wear.

## CLAIMS

1. Process for coating machine parts and tools, preferably of temperature sensitive steels, with high hardness materials of nitrogen and carbon compounds of metals from the group Ti, Zr, Hf, Cr, Ta, W and Nb by reactive cathodic vapourisation of at least one of the said metals in a nitrogen or carbon containing atmosphere under atomisation conditions, wherein metallic intermediate layers of at least one metal from the group Ti, Zr, Hf, Cr, Ta, W, Nb; Al, Ni and Fe are applied by cathodic atomisation under substantially non-reactive conditions between individual layers, comprising each only a fraction of the total coating thickness, of high hardness material from the group TiN, TiC, TiCN; ZrN; HfN, Cr<sub>2</sub>C<sub>3</sub>; TaC, TaN; WN, WC and NbN.
2. Process according to claim 1, wherein the coating is built up from 2 to 100 layers of high hardness material and 1 to 99 metal layers in alternating sequence.
3. Process according to claim 1, wherein a thickness of from 50 to 1000nm is chosen for the individual layers of high hardness material.
4. Process according to claim 1, wherein a thickness of from 5 to 100nm is chosen for the individual metal layers.
5. Process according to claim 1, wherein the ratio of layer thickness of the individual high hardness material layers to that of the individual metal layers is chosen to be between 10:1 and 10:5.
6. Tools, preferably having a base body (substrate) of a temperature sensitive steel and a coating of high hardness material of nitrogen and carbon compounds of metals from the group Ti, Zr, Hf, Cr, Ta, W and Nb, wherein between individual layers, each of only a fraction of the total coating thickness, of high hardness material from the group TiN, TiC, TiCN; ZrN; HfN; CrN, Cr<sub>2</sub>C<sub>3</sub>; TaC, TaN; WN, WC; NbN are arranged metallic intermediate layers from the group Ti, Zr, Hf, Cr, Ta, W, Nb; Al, Ni, Fe.